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Photochemistry of *t*-Butyl Alkyl Ketones in Solution

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Photochemistry of *t*-Butyl Alkyl Ketones in Solution

Sir:

It has been recognized for some time that aliphatic ketones can undergo several distinct types of photochemical reactions. The effects of structure and spin multiplicity of excited states on the competition between these types of reactions, however, are still not completely understood. We have investigated the

Table I. Quantum Yields for the Primary Processes[a]

Compd	ϕ^0	ϕ^S	$\phi_I{}^{S\,b}$	$\phi^S{}_{II}$	$\phi^S{}_{cyc}$	ϕ^T	$\phi^T{}_I$	$\phi^T{}_{II}$	$\phi^T{}_{cyc}$
Ia	0.51	0.18	0.18			0.33	0.33		
Ib[c]	0.59	0.24	0.22	0.02	0.00	0.35	0.35	<0.01	0.00
Ic	0.31	0.14	0.07	0.07	0.00	0.17	0.17	<0.01	<0.01
Acetone							<0.02[d]		
2-Pentanone	0.27	0.03[e]		0.02[e]	<0.01[e]	0.24[e]		0.16[e]	0.08[e]
2-Hexanone[f]	0.33	0.11		0.10	<0.01	0.22		0.15	0.07

[a] Values accurate to at least ±10%. [b] Difference of ϕ^S and $\phi^S{}_{II}$. [c] In the vapor phase at 150°, $\phi^0 = 0.65$, $\phi_I = 0.54$, $\phi_{II} = 0.12$ (C. H. Nicol and J. G. Calvert, *J. Am. Chem. Soc.*, **89**, 1790 (1967)). [d] D. H. Yang, unpublished results; the predominant processes involve hydrogen abstraction from the medium. [e] Reference 5a, adjusted for ϕ^0 value given here. [f] Reference 5c.

photochemistry of *t*-butyl alkyl ketones in solution with the intention of further elucidating the correlation of these factors with their photochemical reactivity.

Irradiation of hexane solutions of *t*-butyl alkyl ketones (0.6–0.8 *M*) (Ia–Ic) with light (3130 Å) results in fragmentation of these ketones by both type I (eq 1) and type II (eq 2) processes,[1] and to a lesser extent in photocyclization (eq 3).[2]

$$t\text{-}C_4H_9COR \xrightarrow{h\nu} i\text{-}C_4H_8 + i\text{-}C_4H_{10} + \text{RCHO} + \text{other products} \quad (1)$$

Ia, R = CH_3; b, R = n-C_3H_7; c, R = n-C_4H_9

IIa, R = CH_3; b, R = n-C_3H_7; c, R = n-C_4H_9

$$t\text{-}C_4H_9COR \xrightarrow{h\nu} t\text{-}C_4H_9COCH_3 + C_2H_3R \quad (2)$$

Ib, c → IIIb, R = H; c, R = CH_3

$$t\text{-}C_4H_9COR \xrightarrow{h\nu} t\text{-}C_4H_9(HO)\overline{CCH_2CH_2CHR} \quad (3)$$

Ic → IVc, R = CH_3

The total quantum yield for disappearance of starting ketone (ϕ^0, Table I) and the product yields were determined by gas chromatography with the aid of a ferrioxalate actinometer.[3] By quenching the triplet state of the three ketones with added piperylene,[4] we observed a rapid decrease in total quantum yield (ϕ) at lower quencher concentrations, followed by a more gradual decrease at higher quencher concentrations (Figure 1). The quantum yields for ketone decomposition *via* singlet excited state (ϕ^S) were determined from the limiting values of ϕ^0/ϕ from Figure 1. The quantum yields for ketone decomposition *via* the triplet state (ϕ^T) were obtained as the differences between ϕ and ϕ^S (*cf.* Table I). The quantum yield for type II process (ϕ_{II}) from Ic was estimated by determining the yield of propylene formation and by comparison of the yield of propylene to the combined yields of isobutane and isobutylene, and ϕ_{II} from Ib was estimated by comparison of the yield of ethylene to the combined yields of isobutane and isobutylene (Table I). The quantum yield for the type II process *via* the singlet excited state was determined by comparing the yield of ethylene or propylene at zero quencher concentration and at higher quencher concentrations (Table I).

t-Butyl *n*-propyl ketone (Ib) is slightly more reactive than pinacolone (Ia), but not solely because of the intervention of the type II process. *n*-Butyl *t*-butyl ketone (Ic) undergoes a type II process several times more efficiently than does *t*-butyl *n*-propyl ketone (Ib); nevertheless, fragmentation by a type I process is drastically reduced. The secondary γ hydrogen enhanced the efficiency of the type II process but reduced the efficiency of the type I process.

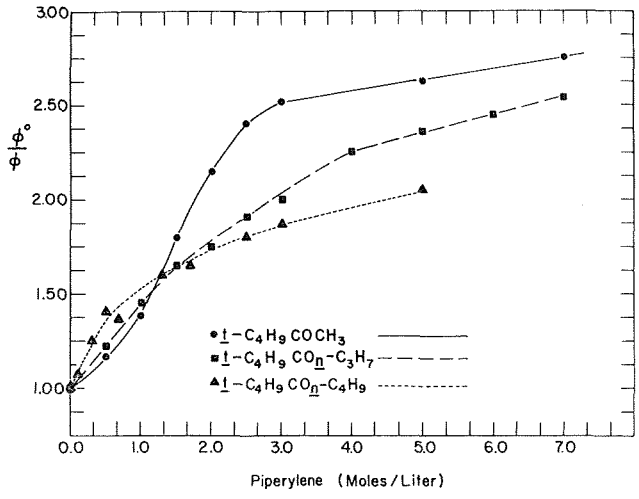

Figure 1.

The present experiments in the condensed phase definitely show that a type I process occurs from both the singlet and the triplet excited states of *t*-butyl alkyl ketones, while a type II process occurs almost exclusively from the singlet excited state of Ib and Ic (Table I). A type II process in the methyl analogs, 2-pentanone and 2-hexanone, however, occurs largely from the triplet state (*cf.* Table I).[5] A very small amount of 1-*t*-butyl-2-methylcyclobutanol (IVc) is detected in the irradiation products of Ic. Coulson and Yang[5c] have shown that cyclobutanol formation from 2-hexanone is predominantly a triplet-state reaction. It is not surprising that little cyclobutanol was formed, since the interaction with the γ hydrogen in the type II process in Ib and Ic is predominantly from the singlet n,π^* state.

Straight-chain aliphatic ketones with γ hydrogens such as 2-alkanones undergo a type II process predominantly if not exclusively under the influence of light, while *t*-butyl alkyl ketones with γ hydrogens (Ib and Ic) undergo mainly type I processes in solution, indicating

(1) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).
(2) N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).
(3) C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956).
(4) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961).
(5) (a) P. J. Wagner and G. S. Hammond, *ibid.*, 87, 4009 (1965); **88**, 1245 (1966); (b) T. J. Dougherty, *ibid.*, **87**, 4011 (1965); (c) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

that the incipient stability of *t*-butyl and acyl radicals dominates the course of the photolysis of *t*-butyl ketones. This situation is not clear in vapor phase photochemistry.[6] The difference between the photochemical behavior of carbonyl compounds in vapor phase and in solution may be attributed to the fact that the excited molecules lose their vibrational energy more rapidly in solution.

We also found that at relatively low piperylene concentrations (0.05 *M*) the quantum yield for photolysis of *t*-butyl alkyl ketones was reduced by only about 10% while the formation of isobutylene was more than 90% suppressed. This observation suggests that isobutylene is formed mainly from free-radical processes.

In summary, we have shown (1) that the type I process in the photolysis of *t*-butyl alkyl ketones is the major reaction mode in solution and arises from both the singlet and the triplet excited states and (2) that the type II process arises predominantly from a singlet excited state.

(6) See Table I, footnote *c*.

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